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REVIEW

A review to recent developments in modification of carbon fiber electrodes

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Abstract   The unique properties of carbon fiber electrodes (CFEs) offer a number of particular advantages for their use in analytical applications. However, some pretreatment is usually necessary for the modification of the carbon surface. One of these methods is enzyme modification, that enzyme reactions in the surface of the electrode can be useful for the certain determinations. Also application of nanoparticles is very useful for modification and gives very interesting responses for the electrode in the determination of various analytes. Electrochemical oxidation of a carbon surface is one of the other methods for modification. With this work the morphology of the surface changes as well as increasing the coverage by various oxygen-containing functional groups. These groups can then interact and bind with other species introduced to the surface. The modification of the surface of carbon fiber electrodes is an interesting topic with many applications in the fields of analytical chemistry, environmental and health science, fuel cell and biofuel cell and many others. In this review article we discussed about the various modification methods for carbon fiber electrodes and applications of these CFEs.
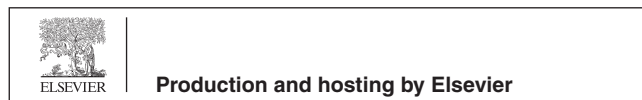
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1. Introduction

Since today various modified electrodes have been used in electroanalytical chemistry (Mohammadzadeh Kakhki, 2013; Mohammad Zadeh Kakhki and Rounaghi, 2011; Rounaghi and Mohammadzadeh Kakhki, 2011; Ronaghi et al., 2011; Ronaghi et al., 2012). Carbon fiber electrodes (CFEs) were first invented in the late 1970s by François Gonon and colleagues (Gonon et al., 1980). The basic manufacturing of their CFE is as follows: the carbon fiber is threaded through a pulled glass tube with a tapered tip, secured in place with a polyester resin and graphite powder mixture forced down into the tip, a contact wire pushed down into the resin and dried 24 h or more. The carbon fiber is cut into a length of 0.5 mm prior to use (Ponchon et al., 1979).

After the invention of CFE, the great potential of the CFE's for various applications was illustrated. The modification of the CFEs can help to resolve many of problems in various determinations (Melissa et al., 2006).

In this article we review the developments of modified carbon fiber electrodes. The modification in various types of CFEs such as enzyme modification, nanoparticle modification, activated carbon fiber cloths and carbon fiber paper has been evaluated.

2. Carbon fiber electrode

2.1. Carbon fiber electrode advantages

The chemically inert carbon fiber (CF) has outstanding mechanical and electrical properties and provides an excellent base electrode for electrophysiological, electrochemical and biosensor applications on a micrometer or perhaps even on a nanometer scale. Activated carbon powders (Mitani et al., 2004; Gamby et al., 2001) and fibers (Leitner et al., 2006; Shiraisgi et al., 2002; Kim et al., 2004) have been widely used as electrode materials due to their high specific surface area and electric conductivity. The carbon fiber electrode has several unique characteristics to give it an advantage over other techniques. Carbon fiber electrodes have the ability to monitor in a subsecond time frame and record in real time. Because they are so small, carbon fiber electrodes are also applicable for using in very small environments, such as a single cell or vesicular volumes, where other devices cannot because they are too big. Besides sensitivity and selectivity, the size of the electrode should be fully considered in order to develop a suitable sensor for in vivo and in situ applications. The electrode should be miniaturized enough to match with the small space in biological microenvironments, such as single cells or certain locations in tissues. In this regard, the carbon fiber microelectrode (CFME) or carbon fiber nanoelectrode (CFNE) with diameter in micrometers and nanometers appears to have great advantages over other electrodes because of their ultra-small size. Furthermore, the fast response time and the excellent biocompatibility of these electrodes make them a powerful tool for real-time monitoring of biological events with high temporal and spatial resolution.

On top of that, carbon fiber electrodes are also excellent devices for greater sensitivity and selectivity by making electrode modifications for the analyte of interest. In addition, carbon fiber electrodes provide a wider range of detectable species, again by simply making slight modifications.

2.2. Modification of carbon fiber electrodes

Modified electrodes are the most interesting tools for the applications in the electrochemical analysis (Mohammadzadeh Kakhki, 2013; Mohammad Zadeh Kakhki and Rounaghi, 2011; Rounaghi and Mohammadzadeh Kakhki, 2011; Ronaghi et al., 2011, 2012). The carbon fiber is readily available and useful material to prepare the modified electrode. Fibers facilitate work in small volumes of solutions while retaining a large electrode surface area (Bismarck et al., 2001, 2002; Kumru et al., 2001; Sarac et al., 2001).

In a report Nilesh Sathe et al. Sathe and Gerardine (2006), have evaluated the carbon fiber electrodes prepared by plating of noble metals (Pt, Rh, Pt–Rh, Pt–Ir, Pt–Ir–Rh) on carbon fibers for the electrolysis of coal and graphite under galvanostatic conditions. Graphite was used as a baseline to compare its performance with coal. The electrodes were tested on a sandwich configuration coal electrolytic cell (CEC) designed to reduce the ohmic resistance of the system. Among Pt, Rh, Pt–Rh, Pt–Ir, and Pt–Ir–Rh electrodes with the same loading (5 mg cm^{-1} of fiber bundle), Pt and Pt–Ir seemed to produce the highest CO_2 Faradic efficiency. Fig. 1 shows a schematic diagram of the procedure that was used for the fabrication of the electrodes. The carbon fibers were wound on the titanium gauze. Typically 34 cm long bundles of fibers (with approximately 6000 fibers per bundle) were used to ensure a uniform coverage of titanium gauze. After winding on the gauze, the ends of these fibers were combined together and then tighten on the stem of the electrode. These fibers were then fixed to the stem with the help of a small titanium clip. The electrodes were cleaned with acetone to remove greasy compounds and they were weighed before and after plating. Deposition of a metal film of silver, gold, or copper on the surface of a graphitized carbon fiber has been shown to enhance the CV peak height of the Li intercalation/deintercalation reaction in the carbon, implying a reaction rate enhancement. The peak height of the anodic peak of the CV changes with the change in thickness. Gold and copper gave the highest peak for the thinnest film, while silver showed a complicated behavior where a contribution of changes in the crystal orientation depending on the film thickness must be taken into consideration. The enhancement effect was elucidated based on two factors, i.e. an electrical conductivity increase and formation of a suitable solid electrolyte interphase (SEI) on the surface of the silver film (Suzuki et al., 2002). In Fig. 2, the SEM
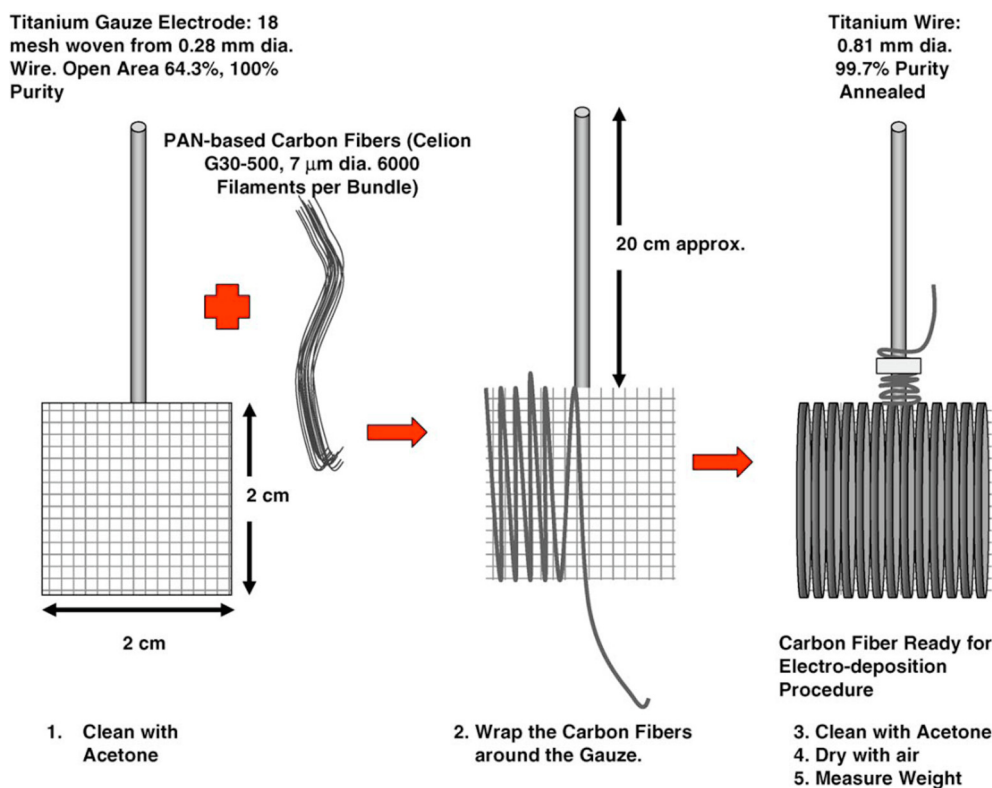
Figure 1 Schematic representation of the procedure used for the preparation of the carbon fiber electrodes (originally drawn by Elizabeth Cellar, undergraduate research student at the EERL Ohio University). Titanium gauze is used as a current collector to increase the electronic conductivity of the fibers.
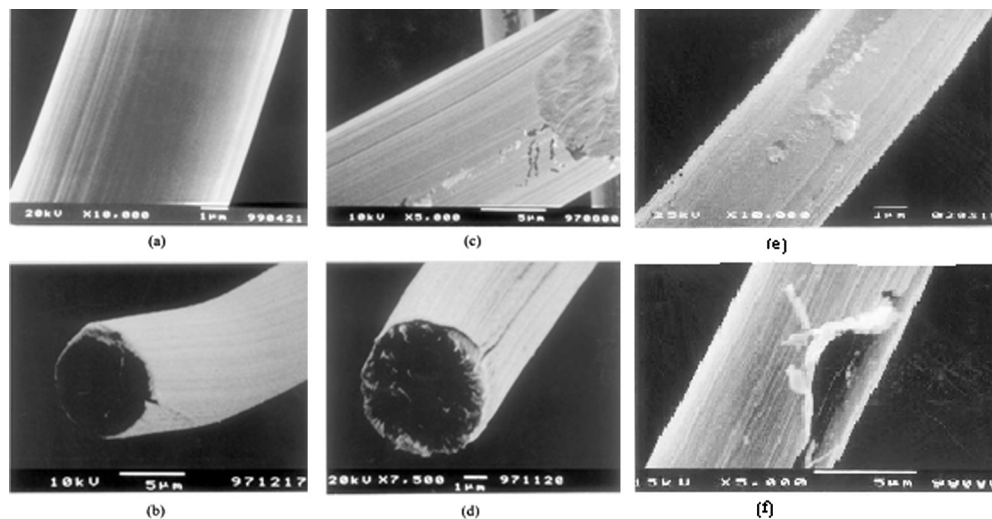

Figure 2 SEM photographs of carbon fibers covered with: (a) a 200 Å thick, and (b) a 500 Å thick copper film; (c) a 200 Å thick, and (d) a 500 Å thick gold film; (e) a 200 Å thick and (f) a 450 Å thick silver film.

images of the carbon fibers covered with the vacuum deposited copper, gold and silver film are illustrated. The figure shows that the carbon surface appears to be covered entirely with a compact metal film.

2.2.1. Enzyme modification
One of the methods that has been used for the modification of carbon fibers is enzyme modification. In a work(Liu et al.,

2010) a lactate microbiosensor based on Prussian Blue (PB)-modified carbon fiber electrodes (CFEs) was developed that allows the detection of enzyme-generated hydrogen peroxide at a low applied potential (~0 V against SCE), contrasting the high over potential used in many previous designs based on platinum transducers (~0.7 V). The results show that this microbiosensor design is well suited to exploring the role of lactate in brain extracellular fluid. This approach allows the

detection of H_2O_2 enzymatically generated in the biosensor surface layer at low applied potential. After optimizing the protocol to modify the CFEs with this electrocatalytic compound (PB), the next step was its modification with lactate oxidase. In this context, biosensor responses were honed to the special conditions needed for physiological applications such as: sensitivity, selectivity, operational linear range, and biocompatibility. Finally, an optimized lactate biosensor is presented and some in vivo results shown to illustrate its application in the study of lactate and oxygen in the brain during neuronal activation.

In the other report a glucose/dioxygen hybrid enzyme-Pt micro-biofuel cell (BFC) was investigated (Sales et al., 2013). In this miniaturized BFC, a flexible carbon fiber (FCF) microelectrode modified with neutral red redox mediator and glucose oxidase was used as the bioanode, and an FCF modified with platinum nanoparticles stabilized on PAMAM-G4 dendrimer was used as the cathode. In vitro experiments showed high electrocatalytic performance with an open circuit voltage (OCV) of 400 mV, a maximum current density of 2700 $\mu A\,cm^{-2}$ at 0.0 V and a maximum output power of 200 $\mu W\,cm^{-2}$ at 250 mV. Under physiological conditions, glucose from rat blood is used as a fuel in anodic reactions and dissolved molecular oxygen is used as the oxidizing agent on the cathode. For in vivo experiments, the BFC was inserted into the jugular vein of a living rat (Rattus novergicus) using a catheter (internal diameter 0.5 mm). The power density of the implantable BFC was evaluated over a period of 24 h, and an OCV of 125 mV with a maximum power density of 95 $\mu W\,cm^{-2}$ was obtained at 80 mV.

Carbon fiber paper (CFP) is an electrically conducting carbon paper that is formed by laminating the randomly arranged short carbon fibers in a two-dimensional sheet. The carbon paper made from carbon fiber felt displays good processing properties and is thought to be potential electrode material. However, after high temperature heat-treating the carbonization shrinkage becomes large, leading to the change in the

Figure 3 Fabrication and characterization of CFP electrode. (A) Schematic showing the fabrication of a CFP-based electrode. (B) The cyclic voltammograms of ferricyanide on the CFP (curve a) and the CFPP (curve b) electrodes were determined in a reaction chamber containing PBS, pH 6.5 within a potential between −0.6 V and 0.8 V vs. Ag/AgCl. The scan rate was 120 mV s^{-1}.

structures of the fiber and matrix and the closing of porosity. In addition, resin carbon is difficult to graphitize. All these factors can deteriorate the conductive properties and the thermal performance as well as the mechanical properties of the carbon paper. In order to further improve the comprehensive performance of carbon paper, considerable efforts have been devoted to the decoration and modification (Liu et al., 2008; Mathur et al., 2006; Saha et al., 2009, 2007). CFP was found in a study to exhibit great potential in the fabrication of biosensors. However, untreated CFP is very hydrophobic and exhibits a relatively low response to electroactive agents. Once treated with nitrogen plasma, CFP becomes hydrophilic and has greatly improved its electrochemical properties, such as a high rate of electron transfer and the existence of quasi-reversible processes. A CFP-based tyrosinase biosensor was fabricated to explore its potential in the development of an amperometric biosensor. Interestingly, the CFP-based tyrosinase biosensor exhibited a high sensitivity to phenolic compounds; the working electrode was prepared as presented in Fig. 3. A. Briefly, a supporting plastic strip (0.3 cm × 2.4 cm) was first covered by a piece of copper foil adhesive tape (0.3 cm × 1.9 cm) to form a conducting surface. The remaining area (0.3 cm × 0.5 cm) was then covered with Teflon glue to form an insulating layer. CFP (0.3 cm × 1.4 cm) was then partially bound on the supporting strip (0.7 cm in length) at the side covered with Teflon film, allowing a 0.2 cm wide area of CFP to directly contact with copper foil. The remaining part of the CFP (0.7 cm in length) overhung from the supporting strip and acted as a working electrode. The surface of CFP outside the working area (0.3 cm × 0.7 cm) was insulated with the Teflon film to prevent unwanted redox reactions.

2.2.2. Nanoparticle modification

Nowadays the application of nano particles as a suitable modifier in very interested in for researchers. In a work carbon nanofibers were produced (Engel et al., 2013) by the electrospinning of polyacrylonitrile solution followed by convenient thermal treatments (stabilization followed by carbonization at 1000, 1200 and 1400 °C), and carbon nanotubes were adsorbed on the surfaces of the fibers by a dipping method. The electrochemical properties were evaluated through cyclic voltammetry, where the influence of the carbonization temperature of the fibers and the beneficial contribution of the carbon nanotubes were observed through the reversibility and size of the redox peaks of $K_3Fe(CN)_6$ versus Ag/AgCl. Subsequently, redox enzymes were immobilized on the electrodes and the electroreduction of oxygen to water was realized as a test of their efficiency as biocathodes. Due to the fibrous and porous structure of these new electrodes, and to the fact that carbon nanotubes may have the ability to promote electron transfer reactions of redox biomolecules, the new electrodes developed were capable of producing higher current densities than an electrode composed only of electrospun carbon fibers.

In an interesting report, a nickel nanoparticle-loaded carbon fiber paste (NiCFP) electrode for enzyme free determination of ethanol was reported (Salazar et al., 2012). An electrospinning technique was used to prepare the NiCF composite with large amounts of spherical nanoparticles firmly embedded in carbon fibers (CF). In application to electroanalysis of ethanol, the NiCFP electrode exhibited high amperometric response and good operational stability. The calibration curve was linear
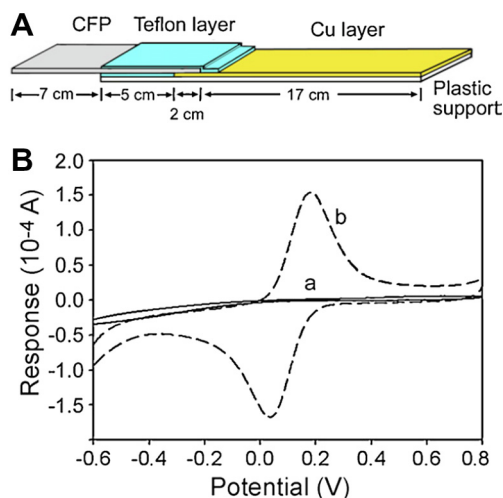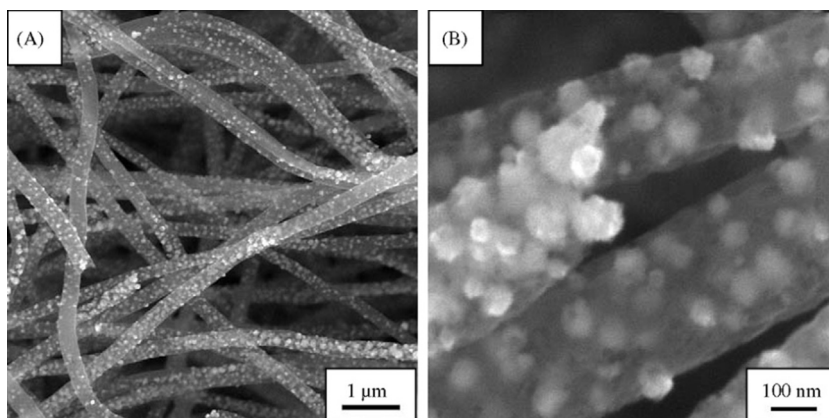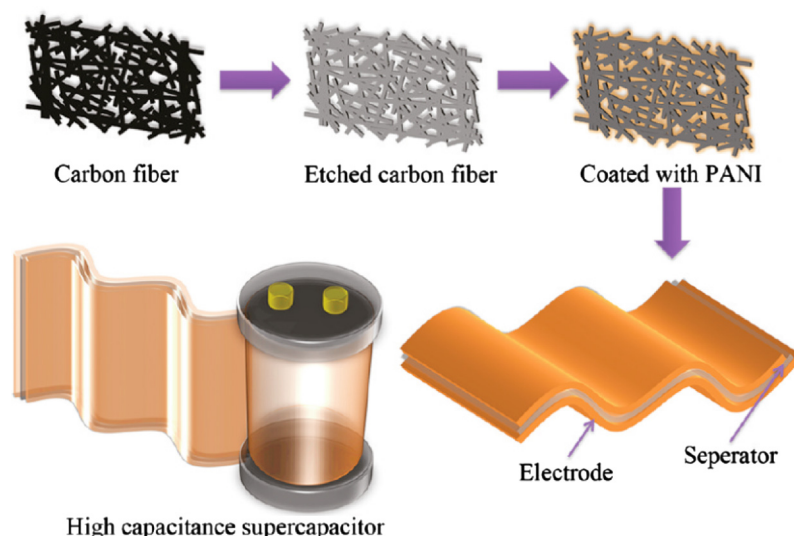
Figure 4 SEM images of the NiCF composite at (A) low and (B) high magnification (Priyanka et al., 2009).

Scheme 1 Procedure for the preparation of carbon electrodes and supercapacitor. Carbon fiber cloth was first etched by electro-etching. The etched carbon fiber cloth was then coated with PANI by electrodeposition. This kind of electrodes can be made into flexible structure that can be rolled into coiled foils.

up to 87.5 mM with a detection limit of 0.25 mM, which is superior to that obtained with other transition metal based electrodes. The attractive analytical performance and simple preparation method make this novel material promising for the development of effective enzyme-free sensors [+]. The morphology of the prepared NiCF composite was investigated by SEM (Fig. 4). As shown in Fig. 4A, large amounts of nanoparticles are well dispersed on the CF, which have a diameter of 200–400 nm and a length of tens of micrometers. The high-magnification image indicates that the nanoparticles with a diameter of about 50 nm are firmly embedded in the CF matrix and hardly detach from the composite (Fig. 4B).

Also carbon fiber electrode (CFE) modified by graphene flowers and used to simultaneously determine ascorbic acid (AA), dopamine (DA) and uric acid (UA) Du et al., 2014. SEM images showed that beautiful and layer-petal graphene flowers homogeneously bloomed on the surface of CFE. Moreover, sharp and obvious oxidation peaks were found at the obtained electrode when compared with CFE and glassy carbon electrode (GCE) for the oxidation of AA, DA and UA.

The obtained electrode showed satisfactory results when applied to the determination of AA, DA and UA in urine and serum samples.

Carbon fiber clothes are a promising material for electrodes of supercapacitors owing to their unique 3-D structure, high surface area, remarkable chemical stability, and electrical conductivity. In a study(Cheng et al., 2011), electro-etched carbon fiber cloth is explored as an electrode for supercapacitors by coating polyaniline nanowires. The scheme of the procedure is shown in Scheme 1. The as-prepared electro-etched carbon fiber cloth and polyaniline nanowires, which were characterized by scanning electron microscopy and transmission electron microscopy, were assembled into supercapacitors. The polyaniline nanowires can reach a mass-normalized specific capacitance of 673 F/g and an area-normalized specific capacitance of 3.5 F/cm². The electro-etching process is very important for making the carbon fiber cloth electrodes effective and efficient. First, the electro-etching process can greatly increase the surface area of the carbon fiber cloth. Second, the etching process can increase the hydrophilicity of the carbon fiber

cloth and make it easier for uniform PANI coating. Moreover, the coating of PANI can decrease the electrical resistance of the electrodes. The etching and coating of single carbon fiber using the same processing method were also studied. The single fiber shows almost the same specific capacitance as the carbon fiber cloth of the same coating density, indicating good accessibility of etched carbon fiber cloth electrode.

In the other study, a high-performance biofuel cell construction based on the covalent immobilizing of glucose oxidase (GOx) on chitosan-coated carbon cloth was developed (Yang and Shieh, 2013). The chitosan was coated by the coagulation of an aqueous chitosan solution on the carbon cloth surface. The GOx was coupled to chitosan using N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide (EDC) and N-hydroxysuccinimide (NHS) as the condensing agents. Response surface methodology (RSM) and Box-Behnken design were employed to search for the optimal conditions, and to understand the significance of the factors affecting the activity of immobilized GOx. Based on the regression model, the carbon cloth electrodes with various GOx activities were prepared, and the effect of GOx activity on the power density generated from the biofuel cell was investigated. Taking the above results into consideration, this enzyme immobilization technique could be key to the production of high-powered, stable and cost-effective commercial enzymatic biofuel cells in the future.

Also a simple, scalable and cost effective process for the preparation of Carbon nanotube network modified carbon fiber paper electrodes via a CVD process that can be directly used as the anode material in a Li-ion battery was developed (Chen et al., 2009). This composite electrode showed a significant fully reversible capacity. The resultant CNT/CFP electrodes have created a superior stable electrode material for use in electrochemically driven alternative energy applications such as batteries, supercapacitors or fuel cell devices.

Ultraporous Pd nanocrystals for electrocatalysis applications were fabricated using a direct electrodeposition method on three differing carbon supports: flexible carbon fiber paper (CFP), and CFP modified with either graphene oxide nanosheets or their chemically reduced forms using a simple spray coating technique (Sawangphruk et al., 2013). The electrocatalytic activity of these electrodes was investigated for the direct electro-oxidation reaction of methanol in alkaline media. Pd deposited on the CFP modified with reduced graphene oxide (rGO) has excellent poisoning tolerance to carbonaceous species and a significantly better catalytic activity toward methanol oxidation than the other two catalyst support materials. It is believed that the collaborative effects due to the three-dimensional ultraporous Pd nanocrystals and fast electron transfer owing to high conductivity of rGO nanosheets play an important role in enhancing the catalytic performance of Pd/rGO/CFP toward methanol oxidation in alkali media.

In the CFMEs that usually constructed in cylindrical shape. They showed high response to analyte owing to their large electrode area. However, the current noise from the electrodes was also big and the detection limit was hereby limited. The carbon fiber microdisk electrodes can be prepared by sealing short lengths of carbon fiber directly into glass. The microelectrode surface was polished mechanically with graded alumina powder of different sizes on a polishing cloth. In order to improve the repeatability of the measurements, an electrochemical cleaning of the electrode surface was also made by cycling the potential several times in buffer a, until the blank cyclic voltammograms were reproducible. These electrodes has been used for low concentration determination of the metronidazole(Bartletta et al., 2005) in buffer or untreated urine at the carbon fiber microelectrode with detection limits of 5×10^{-7} and 1×10^{-6} mol dm^{-3}, respectively using square wave adsorptive stripping voltammetry.

In a paper a NO electrochemical microsensor, which is fabricated by modifying the surface of a carbon fiber microdisk electrode (CFMDE, diameter: 5–7 μm) with single-walled carbon nanotubes (SWNTs) and Nafion membrane, is reported (Du et al., 2008). The modification of SWNTs dramatically improves the sensitivity of CFMDEs, and the detection limit for NO is 4.3 nM that is nearly 10 times lower than that from the bare one and lower than most NO electrochemical sensors reported before. The Nafion membrane offers a good barrier to some interferents such as nitrite and ascorbic acid without losing response speed to NO. The sensor has been successfully applied to the measurement of NO release from single isolated human umbilical vein endothelial cells (HUVECs). Real-time amperometric data show that the addition of l-arginine (l-arg) or acetylcholine (ACh) can cause a quick increase in NO production with a maximum concentration of 232 ± 44 nM ($n = 5$) and 159 ± 29 nM ($n = 5$), respectively.

Amatore et al. made a NO microsensor (Amatore et al., 2006) by platinizing the surface of a carbon fiber microdisk electrode and successfully used the electrode for the direct and in situ electrochemical detection of NO release from neurons into ex vivo cerebellum slices. The disk shape and ultramicro size of our sensor allow direct measurements near the surface of a single isolated cell in real time. A bare CFMDE is not sensitive enough to the nitric oxide existing in biological systems. Additionally, it may suffer interference from some electroactive substances, such as nitrite and ascorbic acid. Therefore, CFMDEs were modified by SWNTs and Nafion before use. In order to modify the surface of the CFMDE instead of the whole surface of the sensor, a novel method was developed for modification. A CFMDE was connected to the EPC10 patch clamp amplifier and hung vertically above the modifying solution by a micromanipulator as shown in Fig. 5A(a). Ag/AgCl electrode was used as the reference electrode and was put into the modifying solution. Start the program "PULSE", and give a double pulse test with width of 5 ms and amplitude of 10 mV (both the width and the amplitude could be altered without changing the wave shape of the resulting signal) to the CFMDE. The signal display provided by an oscilloscope-like window represented current change with time. At first, the CFMDE was hung in the air so that no current would flow because the resistance in the circuit was infinite (Fig. 5A, b), and three fast peaks were visible at the start and the end of the pulse as a result of stray capacitance within the CFMDE. Then, the CFMDE was moved downward and gradually close to the surface of the modifying solution until it just touched the solution (Fig. 5A, c) by using micromanipulator whose minimum step was 1 μm. At the moment, the electric circuit was completed through the electrode and the modifying solution. Both the capacitance and the resistance within the electrode changed, which resulted in the obvious change in the current trace (Fig. 5A, d). Under this guidance, we stopped moving down the CFMDE and lifted it up immediately (Fig. 5A, e). The length of time for each dipping was about 1 s. Let the tip dry in the air and then repeat the above step twice. After the modification of SWNTs, the
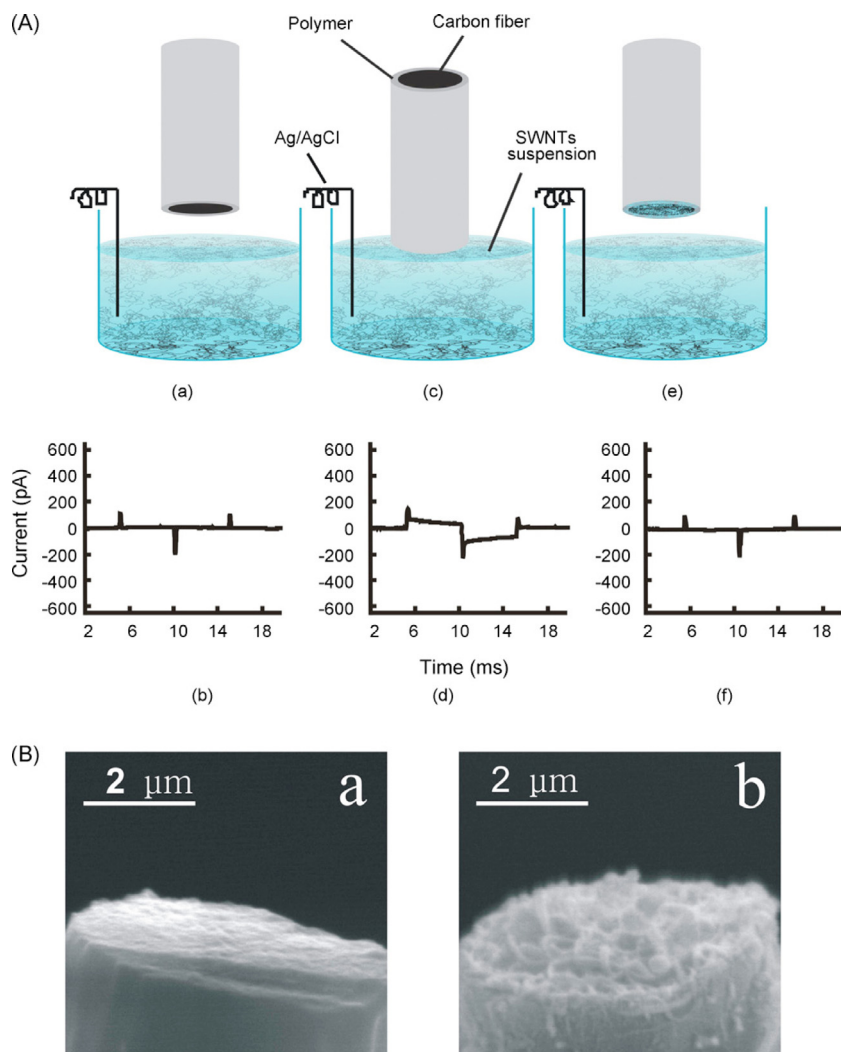
Figure 5 (A) (a, c, e) Schematic diagram illustrating the process of modifying the CFMDE. (b, d, f) The signal display provided by an oscilloscope-like window in 'PLUSE' corresponding with three processes in (a), (c), and (e), respectively. (B) SEM images of (a) the surface of a carbon fiber microdisk electrode (CFMDE) and (b) the surface of an SWNTs/Nafion modified CFMDE.

electrode was coated by Nafion in the same way with 0.5% Nafion–ethanol solution.

This new sensor exhibited excellent electrochemical characteristics for NO detection owing to much larger available internal surface per external geometric area of SWNTs. The sensitivity of the sensor for NO increased 10 times compared to that from the unmodified CFMDEs.

Also Sn nanoparticle/porous carbon composites were prepared by impregnating the surface of porous carbon with a tin salt and subsequent heating (Egashir et al., 2002). The particle size of metallic tin in this composite was 20–40 nm and was controlled by choosing porous carbon with a appropriate surface structure. Tin nanoparticles existing on an ACF surface provided as high as 100 mA h g^{-1} of additional capacities for the high rate charge–discharge cycle, and showed good cycle ability when using adequate Sn amount and ACF the pore volume. Though the reversible capacities are still insufficient at the present level, this kind of composite material is expected to be useful as a negative electrode for advanced lithium batteries by further preparation conditions improvement.

Porous conducting carbon paper has been identified as the most promising material, not only because of its high conductivity that allows easy flow of electrons but also because of its fine porosity that allows uniform distribution of the reactant gases over its surface. The high mechanical strength of the carbon paper provides mechanical integrity to the MEA. Because of the strong fiber matrix interaction during the curing and carbonization cycles (with the commercially available fibers), large volume shrinkage occurred along the thickness of the sample which not only resulted in the decrease in the porosity of the samples but also in a non-uniform pore size distribution (PSD). In a study Maheswari et al., 2009 two different approaches of controlling the fiber–matrix interactions (and hence the porosity and pore size distribution) by modifying the surface of carbon fibers has been reported. In the first case by using surface cleaned carbon fibers along with the neat fibers (as received commercial fibers) in varying proportions, while in the second case the surface of the carbon fiber has been further modified by MWCNTs coating. References have been cited whereby CNTs have been effectively used as a

catalyst support for better utilization of the later, which in turn leads to increased performance (Saha et al., 2008; Kannan et al., 2009; Rajalakshmi et al., 2005; Carmo et al., 2005; Matsumoto et al., 2004) and durability (Wang et al., 2006) of fuel cell. By this technique significant improvement in the physical and electrical properties of the carbon paper was observed, therefore, a novel technique, of coating controlled amount of MWCNTs on to the carbon fiber surface on a continuous scale has been established. The fiber was coated with nanotubes in a continuous manner using chemical vapor deposition (CVD) process. Ferrocene was used as the source of Fe catalyst whereas toluene was used as hydrocarbon source. The carbon fiber was passed through 12 wt% ferrocene solution and squeezed through a hole of diameter 1 mm, so that it is uniformly coated with ferrocene, prior to its entry into the CVD reactor (Fig. 6).

At the exit end the fiber was collected onto a spool which in turn was connected to a motor that pulls the fiber tow. The pulling speed was adjusted to control residence time of the fiber in the effective reaction zone. The amount of CNT growth was thus controlled. The SEM picture of the fibers clearly shows a uniform coating of MWCNTs on the fiber surface (Fig. 7).

The improved performance can be attributed to the high electrical conductivity and uniform pore size distribution of the carbon paper. Also the use of CNT coated fiber also assisted in maintaining high strength along with introducing flexibility in the paper.

Carbon nanofiber/nanotube (CNF/CNT) composite catalysts grown on carbon felt (CF), prepared from a simple way involving the thermal decomposition of acetylene gas over Ni catalysts, are studied as electrode materials in a vanadium redox flow battery(Park et al., 2013). The electrode with the composite catalyst prepared at 700 °C. this composite electrode in the full cell exhibits substantially improved discharge capacity and energy efficiency by ~64% and by ~25% at 40 mA cm^{-2} and 100 mA cm^{-2}, respectively, compared to untreated CF electrode. This outstanding performance is due to the enhanced surface defect sites of exposed edge plane in CNF and a fast electron transfer rate of in-plane side wall of the CNT.

A facile and cost effective approach has been developed toward electrochemical fabrication of graphene-modified carbon fiber electrode (GE/CFE) to determine the content of uric acid (UA) via cyclic voltammetry (CV) and potentiostatic (i–t) methods Du et al., 2013. The combined merits of GE and CFE endow the electrode with large specific surface area and high electrical conductivity. The advantage of thus obtained
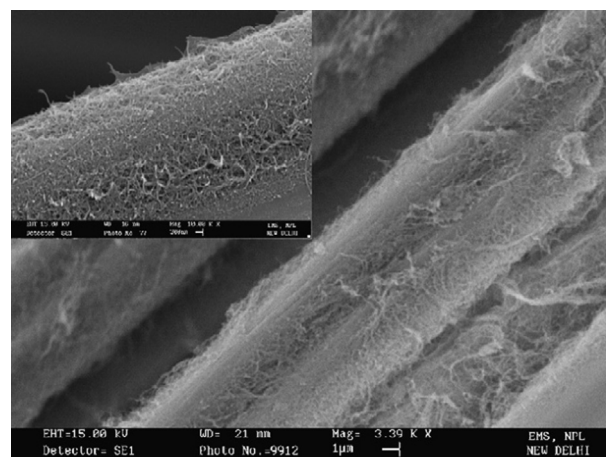

Figure 7 SEM image of the surface of type C carbon fibers. Inset showing SEM image of the carbon fiber preforms prepared with type C carbon fiber, indicating a strong anchoring of MWCNTs with the carbon fiber surface.

GE/CFE for UA detection is supported by its higher peak current intensity and lower oxidation potential compared with those of bare glassy carbon electrode (GCE), bare carbon fiber electrode (CFE), and graphene-modified glassy carbon electrode (GE/GCE). The determination of UA with GE/CFE is highly selective and reproducible, within a relative standard deviation of 2.8%.

Graphene–metal nanoparticles composite has attracted extensive attention in recent years in many fields such as sensor and fuel cells (Li et al., 2007; Lu et al., 2012). Gold nanoparticles, which are usually applied to bimolecular immobilization, have many advantages such as excellent catalytic activity, huge surface area, effective mass transport, and hospitable environment. Furthermore, they can serve on electron tunnel to promote electron exchange at electron/protein interface (Cui and Zhang, 2012; Shanmugasundaram et al., 2011), and thereby gold nanoparticles have found many applications in biosensors (Yue et al., 2012; Kim et al., 2010). Graphene (GE), a one-atom-thick sp2-bonded carbon sheet, has attracted tremendous attention in recent years due to its large amount of edge-plan-like defects and large specific surface area (Luo et al., 2012).

A novel layer-by-layer assembly of graphene sheets and gold nanoparticles modified carbon fiber electrode (GE/Au/GE/CFE) was successfully fabricated and applied to simultaneous determination of dopamine (DA) and uric acid (UA)Du
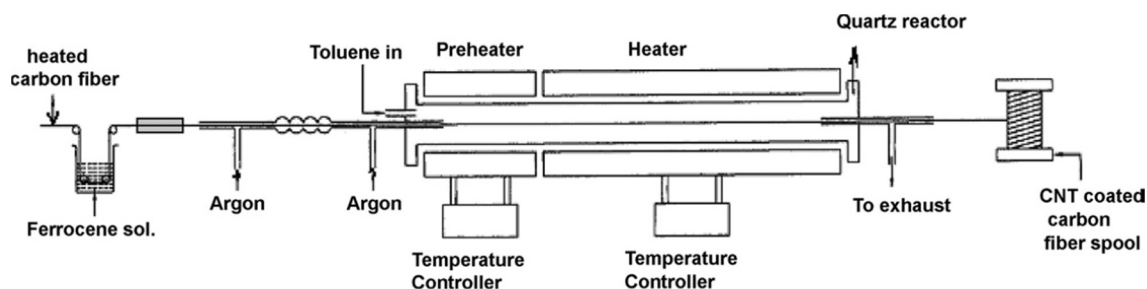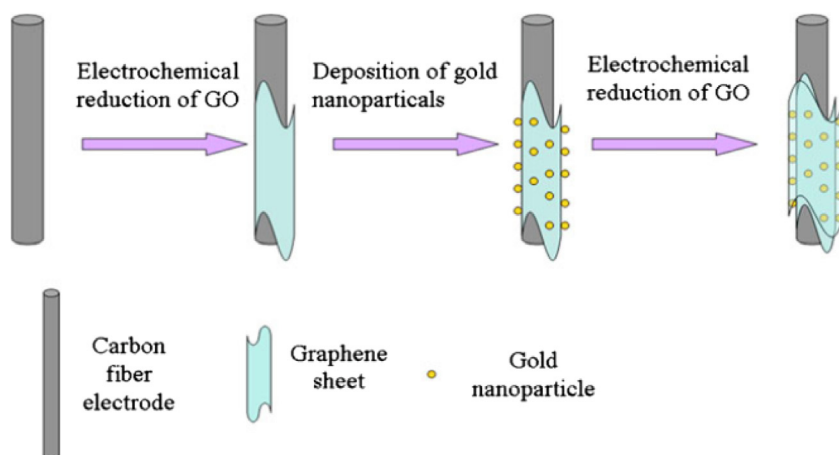

Figure 6 Schematic of the experimental setup for the growth of MWCNT on carbon fiber surface by CVD technique.

Scheme 2 Illustration of the fabrication of GE/Au/GE/CFE.

et al., 2013. A scheme of the process is shown in Scheme 2. The structure of GE/Au/GE/CFE was characterized by scanning electron microscopy (SEM). It was observed that the gold nanoparticles were homogeneously assembled between the two layers of GE sheets. Cyclic voltammetry (CV) measurements elucidate that GE/Au/GE/CFE has higher electrocatalytic activity for the oxidation of DA and UA when compared with graphene modified carbon fiber electrode (GE/CFE), and graphene and gold nanoparticles modified carbon fiber electrode (Au/GE/CFE). Simultaneous determination of UA and DA onGE/Au/GE/CFE was conducted with a differential pulse voltammetry technique, and two well defined and fully resolved anodic oxidation peaks were observed.

The introduction of GE and gold nanoparticles and the structure of GE/Au/GE/CFE increase the effective electroactive surface area, and also enhance the ability of electron transfer. Additionally, the low detection limit and wide detection range evince that the developed electrode is of high selectivity and good reproducibility toward UA and DA determination.

2.2.3. Modification with the activated method

Activated carbon fibers (ACFs) are typical microporous materials with large surface areas and good conductivity along fiber axis. The practical use and applications of activated carbons (ACFs) in many industrial fields and technologies are based on their outstanding physicochemical properties, especially the surface area, the porous texture and the surface chemistry.

Electrochemistry with its unique ability to remove contaminants from solution by adding or withdrawing electrons without introducing any new chemical offers many possibilities for wastewater treatment. In a interesting work, detailed description of electrochemical removal of Fulvic acid (FA)from water using ACF electrodes (Yang et al., 2004) was reported. The proposed mechanism of electrochemical removal of FA is: adsorption of FA on ACF surface-aggregation → FA-desorption → FA aggregates from ACF coagulation → aggregates by $nFe(OH)_2 \cdot mFe(OH)_3$ dissolved from anode. In this work with the understanding of ACF characteristics, a new, safe and promising way to remove organics from water without introducing any added chemical into the system was developed.

The Pd/Sn-modified activated carbon fiber (ACF) electrodes were successfully prepared by the impregnation of Pd^{2+} and Sn^{2+} ions onto ACF, and their electrocatalytic reduction capacity for nitrate ions in water was evaluated in a batch experiment(Wang et al., 2006). The capacity for nitrate reduction depending on Sn content on the electrode and the pH of electrolyte was discussed at length. The results showed that at an applied current density of $1.11 \, \text{mA cm}^{-2}$, nitrate ions in water (solution volume: 400 mL) were reduced from 110 to $3.4 \, \text{mg L}^{-1}$ after 240 min with consecutive change in intermediate nitrite. With the increase of Sn content on the Pd/Sn-modified ACF electrode, the activity for nitrate reduction went up to reach a maximum (at Pd/Sn = 4) and then decreased, while the selectivity to N_2 was depressed. Higher pH value of electrolyte exhibited more suppression effect on the reduction of nitrite than that of nitrate. Additionally, Cu ion in water was found to cover the active sites of the electrode to make the electrode deactivated.

Nitric acid oxidation of activated carbon fabric in combination with calcination in N_2 at different temperatures was conducted to explore the influence of surface carbon–oxygen complexes on the performance of electrochemical capacitors fabricated with the carbon fabric (Nian and Teng, 2002). The specific capacitance of the carbon was found to increase upon oxidation. Surface complex analysis using temperature programmed desorption showed that the double-layer capacitance was enhanced due to the presence of CO-desorbing complexes while CO_2-desorbing complexes exhibited a negative effect. The micropore resistance for ion migration was low for these carbons. A capacitance increase of more than 40% has been achieved, without increasing IR drop, by nitric acid oxidation followed by 450 °C calcination that was shown to remove the majority of the CO_2-desorbing complexes while retaining the CO-desorbing complexes.

Superior over carbon fibers or powders, carbon cloths can be directly used as electrodes. The specific area (1000–3000 m^2/g) Mochida et al., 1992 of ACF is much larger than that of active carbon, and this gives its greater adsorption ability. The use of insulating binder will increase the internal resistance of the electrode sand deteriorate the rate performance of the electric double layer capacitors (EDLCs). In addition, the binders may block some pores of the porous carbons, resulting

in the diminishment of double layer capacitance. Therefore, Activated carbon fiber cloths (ACFC) electrode is expected to exhibit higher capacitance and better rate performance.

In a work (Xu et al., 2007) that the activated carbon fiber cloths were prepared by carbonizing the pre-oxidized polyacrylonitrile (PAN) fabrics between 400 and 900 °C followed by CO_2 activation. All the resultant ACFCs are flexible with good strength. It seems that the yield and porous structure parameters of the ACFCs depend strongly on the carbonization temperature. The carbonization temperature has a marked effect on both the porosity structure and the electrochemical performances of the ACFCs. A moderate carbonization temperature (600 °C) results in higher specific surface area and larger pore size, and hence higher capacitance and better rate capability.

The manufacture of ACFCs by CO_2 activation involves two steps: the carbonization of the precursor under inert atmosphere and the activation of carbonized fabrics in CO_2. In the carbonization step, the resulting chars become richer in carbon and the fundamental porous structure is built by eliminating the noncarbon atoms. Meanwhile, the microcrystalline structure of the chars is rearranged, resulting in a well-ordered structure. The rearrangement hinders the subsequent activation reactions. The carbonization cannot be accomplished at a lower carbonization temperature. On the contrary, carbonization at a higher temperature may make the structure of the carbonized fabrics too ordered to be easily gasified. A moderate carbonization temperature of 600 °C must be the optimal one to balance the two factors to get the most developed porous structure with highest surface area and largest pore size. The specific capacitance of ACFC-600 reaches 208 F g^{-1}. For this ACFC electrode, the *IR* drop is very small. Its capacitance remains 129 F g^{-1} even when the current density increases to 10,000 mA g^{-1}. This is attributed to the good electric conductivity of the activated carbon fiber and the absence of the binder in the ACFC electrodes.

Also in another report (Tabti et al., 2014), the effect and efficiency of the electrochemical treatment in activated carbon cloths was studied .In this work, activated carbon cloths with diameter in the 10–40 μm range with a low tortuosity porous structure and much faster mass-transfer rate compared to powdered activated carbons. The anodic electrochemical treatment of activated carbon cloths in filter press in nitric acid and NaCl electrolytes has been proved to be adequate to produce a controlled oxidation of the carbon fiber surface. In contrast with the usual chemical oxidation treatments, where a high oxidation degree produces a decrease of the microporosity, the porous texture is mostly unaltered after the electro-oxidation treatment. The presence of high amounts of electron-acceptor carboxylic acid groups can be detrimental for the conductivity of activated carbon cloths electrodes. This work shows that electrochemical treatment can be implemented to selectively and quantitatively modify the surface chemistry of activated carbon cloths, preserving both their morphology and their textural properties, and without the need of adding any strong oxidizing agents.

In the other work (Bayram and Ayranci, 2011) the effects of polarization on properties of activated carbon cloth (ACC) have been investigated. Anodic polarization in different electrolytes was found to cause oxidation on ACC. Although the surface textural properties did not change considerably, the changes took place in chemical and electrochemical properties upon anodic polarization were found to be important. Specific surface area, the amount of basic functional groups on the surface and specific capacitance of ACC decreased while the amount of acidic functional groups on the surface, EPZC and EOC increased upon anodic polarization treatment. Cathodic polarization caused a decrease in specific surface area, capacitance, EPZC and EOC of ACC which was taken as an indication of reduction took place on ACC surface.

In two works (Harry et al., 2007, 2006) a viscose-rayon-based activated carbon cloth (ACC) was electrochemically oxidized to enhance its cation sorption capacity. This work introduced weakly acidic functional groups on the surface of the ACC. A significant increase in cation exchange capacity of ACC was obtained by electrochemical oxidation and it increased with the extent of oxidation.

In an interesting work carbon nanofiber (CNF) surfaces were functionalized with oxygen-bearing groups through electrochemical oxidation (Yoon et al., 2011). The electrode was prepared without a binder, allowing easy separation of the functionalized CNFs for subsequent applications. The oxidation of herringbone CNFs was initiated at a relatively low potential at both the anodic and cathodic electrodes, while the O/C atomic ratio remained relatively constant within the range of potentials investigated. The relative concentration of carbonyl and hydroxyl groups increased with increasing potential while the amount of carboxylic groups decreased. Tubular CNFs exhibited low O/C atomic ratios while herringbone CNFs, which have a higher surface area, exhibited the largest ratios. The dispersion of the CNFs in water was much more homogeneous following electrochemical oxidation.

In this case also a surface modification method of carbon fiber by the electrooxidative and -reductive procedures was developed (Ishifune et al., 2005), and successfully prepared the functional carbon fiber electrode bearing cyclodextrin substituents. The carbon fiber surface was oxidized under anodic conditions to introduce phenolic hydroxyl groups on the carbon fiber, and then the resulting oxidized carbon fiber was treated under cathodic conditions in the presence of various kinds of electrophiles such as alkyl halides and alkyl tosylates introducing the alkyl groups on the carbon fiber. The resulting carbon fiber was found to lose the hydrophilicity that was observed in the oxidized carbon fiber because of the alkyl chains introduced on the carbon fiber. These results indicate that the electroreductive modification is much influenced by the electrophilicity of the added electrophiles, and probably attained by the nucleophilic attack of the electrogenerated phenoxide anions on the carbon fiber to the electrophiles forming the ether bonds. This electrochemical surface modification methods are applicable to the fixation of various functional molecules on the carbon fiber by using the corresponding halides and tosylates, for instance, the alkyl amide groups was on the carbon fiber by using haloalkanamides and the CD substituents by using the corresponding tosylate. This modified carbon fibers was used as the electrodes in the determination some of substances.

2.2.4. Modification with construction of carbon fiber paper

Carbon fiber paper (CFP) is an electrically conducting carbon paper that is formed by laminating the randomly arranged short carbon fibers in a two-dimensional sheet. The carbon paper made from carbon fiber felt displays good processing properties and is thought to be potential electrode material.

However, after high temperature heat-treating the carbonization shrinkage becomes large, leading to the change in the structures of the fiber and matrix and the closing of porosity. In addition, resin carbon is difficult to graphitize. All these factors can deteriorate the conductive properties and the thermal performance as well as the mechanical properties of the carbon paper. In order to further improve the comprehensive performance of carbon paper, considerable efforts have been devoted to the decoration and modification (Liu et al., 2008; Saha et al., 2009, 2007). Generally, carbon paper is prepared by a conventional method, in which liquid resin materials are impregnated into carbon precursor and subsequently converted into carbon by heating in an inert atmosphere. Various carbon precursors, such as carbon black, carbon paper, in which carbon nanotubes (CNTs) were uniformly grown on carbon fibers via chemical vapor deposition (CVD) method, and its composites displayed significantly facilitated self-humidifying as the membrane of proton exchange membrane (PEM) fuel cellsDu et al., 2009; Sun et al., 2002; Bordjiba et al., 2007. Recently, XIAO et al. (Yong et al., 2008) developed a new method of preparing carbon fiber paper by CVD, in which the carbon fibers were first heated in an inert atmosphere, then exposed to gaseous organic compounds. Usually, hydrocarbons decompose to deposit a coating of pyrocarbon on the fiber surface. Compared with conventional impregnation method, the CVD method proposed by XIAO has many advantages, such as increase of homogeneity, decrease of shrinkage and cracks and high conductivity.
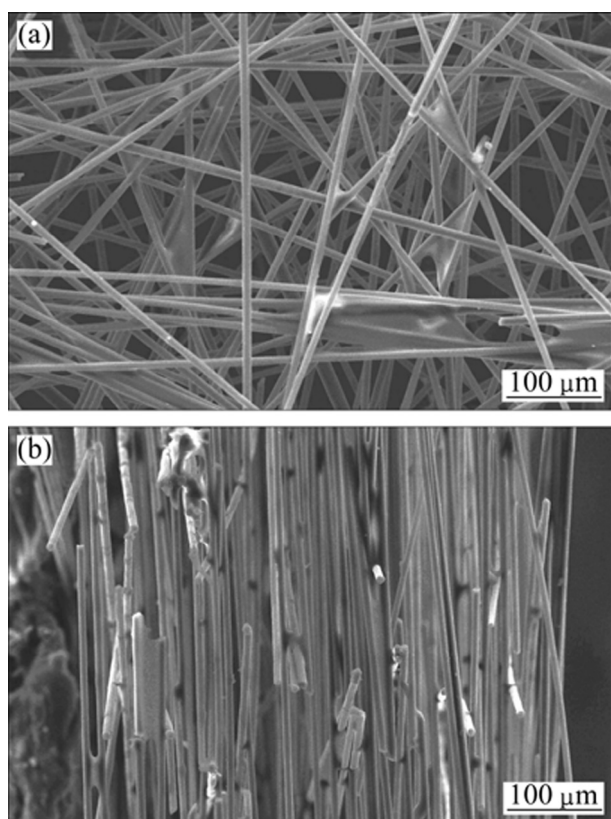
In a report (Yuana et al., 2011) to prepare the conventional carbon paper, PAN-based Toray carbon fibers (T300) and phenolic resin were used as raw materials. The phenolic resin was mixed with carbon fibers to make sure that phenolic resin content was 15% (mass fraction). The carbon fiber felt was prepared by dry paper making technology. SEM micrographs of the surface (Fig. 8(a)) and the cross-section (Fig. 8(b)) of the carbon fiber felt are given in Fig. 8, which had area density of 20 g/m^2 and width of 1000 mm and thickness of 0.5 mm. The carbon fiber felt was cut into pieces of 40 cm × 40 cm and then impregnated with phenolic resin mixture, and dried in an oven at a temperature of 50 °C for 30 min. Two carbon fiber felts were molded together to improve the pore size distribution in the carbon paper, and then they were pressed at 180 °C under 2.5 MPa, thus carbon fiber paper was formed. Finally, the carbon fiber paper was graphitized at 2000 °C in argon with a heating rate of 5 °C/min.

3. Conclusion

Modifications of carbon surfaces are of great importance in electrochemistry and material science. Modification can improve the application range of the CFEs. We can modify the carbon fiber electrodes with enzymes, nanoparticles, the surface activation or carbon fiber paper. The various methods for modification of carbon fiber electrodes have been evaluated in this review article.

Figure 8 SEM micrographs of surface (a) and cross-section (b) of carbon fiber felt.

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